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(54) Title: HAIR COLORING COMPOSITIONS AND METHODS

(57) Abstract: A hair bleaching and coloring composition comprising: (a) an oxidising agent; and (b) an oxidative and/or non-oxidative hair coloring agent; and (c) ammonium carbonate and/or carbamate; wherein the pH of the composition lies in the range of from about 7 to about 9. The products can provide excellent hair coloring, a wide variety of shades, good grey coverage, reduced skin irritation and hair damage and reduced odor.

Hair Coloring Compositions and Methods

Technical Field

This invention relates to hair coloring compositions and processes for coloring hair, and more especially to hair coloring compositions which provide both bleaching and coloring to the hair from a single composition.

Background of the Invention

The desire to alter the color of human hair is not a facet of modern times. Since the days of the Roman Empire the color of human hair has been routinely altered to accommodate the changes of fashion and style. However the attainment of precise initial colors which are retained by the hair for a desirable period has remained a more elusive goal. The difficulties in the development of hair coloring compositions which can deliver precise long-lasting colors are in part due to the inherent structure of the hair itself and in part due to the necessary conditions of effective hair coloration processes. Common difficulties with conventional hair coloring compositions include color fade, wash fade, irregular dye uptake, hair damage and brittleness, skin irritation, odor and skin staining.

Over the years significant effort has been directed towards the elimination of many of the problems associated with the dyeing of human hair. Various approaches to hair dyeing have been developed, these include, direct action dyes, natural dyes, metallic dyes and oxidative dyes.

To color human or animal hair using oxidative dye technology the hair is generally treated with a mixture of oxidative hair coloring agents and an oxidising agent. Hydrogen peroxide is the most commonly used oxidising agent. Oxidative hair coloring agents and peroxygen oxidising agents can be used to deliver a variety of hair colors to the hair. However substantial improvement is needed to provide increased flexibility in the variety of hair shades which can be obtained. In general, oxidative hair dye compositions have been used to color/darken the hair and bleach compositions have been used to bleach/lighten the hair. In order to increase the variety of colours beyond that which is available by separate bleach and color compositions, it has been necessary in the

past to carry out a 2-step process by which the hair undergoes a bleaching step with a bleaching composition containing persulphate, followed by a coloring step with a separate coloring composition. A two-step process however can be inconvenient and time-consuming. It has not been possible to include persulphate in a composition together with oxidative coloring agents due to incompatability of the persulphate and oxidative dye components. It is also possible to provide some limited bleaching/lightening from a coloring composition by using ammonia or peroxide. However such a composition can suffer from undesirable odor and insufficient bleaching ability. It would therefore be desirable to deliver both efficient bleaching and coloring from a single composition.

Typically, hair coloring compositions containing oxidative hair coloring agents are formulated at high pH (from about pH 9 to about pH 12) and commonly contain, in addition to the oxidative hair coloring agents and an inorganic peroxygen oxidising agent, peroxide activating agents and a variety of additional cosmetic, coloring agent and peroxygen oxidising agent stabilising agents. It is also known that enhanced oxidative hair coloring agent oxidation can be achieved via the use of a hair swelling agent (HSA). Such HSA's enhance the oxidising and coloring process by swelling the hair fibres to aid both the diffusion of the peroxygen oxidising agent and the oxidative hair coloring agents into the hair and enabling faster, more thorough dye oxidisation and hair coloring. A common HSA is an aqueous (alkaline) solution containing a source of ammonia, such as ammonium hydroxide. However ammonia can cause skin irritation and in addition has an undesirable odour and can cause lacrimatory effects.

Thus, it would be desirable to develop a hair bleaching and coloring composition having desirable odor characteristics comprising oxidative hair coloring agents which delivers improved hair coloring benefits and variety in hair shades without the need for an HSA.

There is also a need for a hair coloring and bleaching composition which reduces damage to the hair and which reduces irritation to the skin of the user. There is also a need for a hair coloring and bleaching composition which provides effective grey hair coverage.

Compounds which produce HCO_3^- ions on dissolution in water are known for use in hair dye compositions. EP-A-435,012 discloses a number of compounds which produce HCO_3^- ions, namely Na_2CO_3, $NaHCO_3$, K_2CO_3, $KHCO_3$, $(NH_4)_2CO_3$, NH_4HCO_3, $CaCO_3$ and $Ca(HCO_3^-)_2$.

It has now been found that a combination of oxidising agents with one or more oxidative or non-oxidative hair coloring agents and ammonium carbonate and/or ammonium carbamate at a pH of from about 7 to about 9, in hair coloring compositions can deliver excellent initial hair bleaching and coloring in combination with improved flexibility and variety of shades, reduced odor, reduced skin irritation and hair damage and effective grey hair coverage without the need for substantial amounts of buffering agents, pH modifiers or hair swelling agents.

All percentages are by weight of the final compositions in the form intended to be used unless specified otherwise.

Summary of the Invention

The subject of the present invention is a hair bleaching and coloring composition suitable for the treatment of human or animal hair.

According to one aspect of the present invention, there is provided a hair bleaching and coloring composition comprising:

(a) an oxidising agent;

(b) an oxidative and/or non-oxidative hair coloring agent;

(c) ammonium carbonate and/or ammonium carbamate;

wherein the pH of the composition is from about 7 to about 9.

It is to be understood that the percentage weights of the composition components herein are expressed in terms of the total composition, and includes the composition in the form of intended use.

According to a further aspect of the present invention, there is provided a method for bleaching and coloring hair wherein a hair bleaching and coloring composition is applied directly to the hair and wherein the hair bleaching and coloring composition comprises:

(a) an oxidising agent;

(b) an oxidative and/or non-oxidative hair coloring agent;

(c) ammonium carbonate and/or ammonium carbamate;

wherein the pH of the composition is from about 7 to about 9.

According to yet another aspect of the present invention, there is provided a kit comprising a first component and a second component, the first component comprising an oxidising agent, and the second component comprising an oxidative and/or non-oxidative hair coloring agent in combination with ammonium carbonate and/or ammonium carbamate.

Detailed Description of the Invention

As used herein the term 'hair' to be treated may be 'living' i.e. on a living body or may be 'non-living' i.e. in a wig, hairpiece or other aggregation of non-living fibres, such as though used in textiles and fabrics. Mammalian, preferably human hair is preferred. However wool, fur and other melanin containing fibres are suitable substrates for the compositions according to the present invention.

As used herein the term 'hair bleaching and coloring composition' is used in the broad sense in that it is intended to encompass compositions containing the combinations herein of an oxidising agent, an oxidative and/or non-oxidative coloring agent and ammonium carbonate and/or ammonium carbamate, wherein the composition has a pH of from about 7 to about 9. Moreover, it is also intended to include complex compositions which contain other components which may or may not be active ingredients. Thus, the term 'hair bleaching and coloring composition' is intended to apply to compositions which contain, in addition to a mixture of active oxidising agents, coloring agents and ammonium carbonate and/or ammonium carbamate, such things as, by way of example, oxidising aids, sequestrants, stabilisers, thickeners, buffers, carriers, surfactants, solvents, antioxidants, polymers, and conditioners.

Oxidising Agents

The compositions of the invention comprise as an essential feature at least one oxidising agent, which may be an inorganic or organic oxidising agent. The oxidising agent is preferably present at a level of from about 0.01% to about 10%, preferably from about 0.01% to about 6%, more preferably from about 1% to about 4% by weight of composition.

Inorganic Oxidising Agents

A preferred oxidising agent for use herein is an inorganic peroxygen oxidising agent. The inorganic peroxygen oxidising agent should be safe and effective for use in the compositions herein. Preferably, the inorganic peroxygen oxidising agents suitable for use herein will be soluble in the compositions according to the present invention when in liquid form or in the form intended to be used. Preferably, inorganic peroxygen oxidising agents suitable for use herein will be water-soluble. Water soluble oxidising agents as defined herein means agents which have a solubility to the extent of about 10g in 1000ml of deionised water at 25°C ("Chemistry" C. E. Mortimer. 5th Edn. p277).

The inorganic peroxygen oxidising agents useful herein are generally inorganic peroxygen materials capable of yielding peroxide in an aqueous solution. Inorganic peroxygen oxidising agents are well known in the art and include hydrogen peroxide, inorganic alkali metal peroxides such as sodium periodate, sodium perbromate and sodium peroxide, and inorganic perhydrate salt oxidising compounds, such as the alkali metal salts of perborates, percarbonates, perphosphates, persilicates, persulphates and the like. These inorganic perhydrate salts may be incorporated as monohydrates, tetrahydrates etc. Mixtures of two or more of such inorganic peroxygen oxidising agents can be used if desired. While alkali metal bromates and iodates are suitable for use herein the bromates are preferred. Highly preferred for use in the compositions according to the present invention is hydrogen peroxide.

It has been found that by using the compositions of the present invention, it is possible to deliver effective hair bleaching and colouring without needing to use ammonia, hence there being no ammonia related odor or skin irritation negatives associated with these compositions.

In preferred compositions according to the present invention the inorganic peroxygen oxidising agent is present at a level of from about 0.01% to less than about 6%, preferably

from about 0.01% to about 4%, more preferably from about 1% to about 4%, more preferably from about 2% to about 3% by weight of composition.

Preformed organic peroxyacid

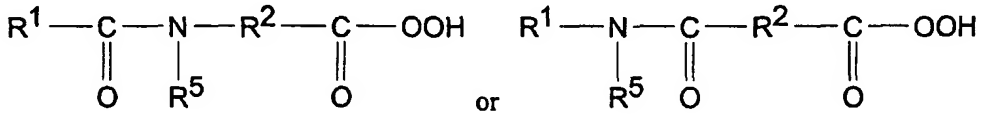
The compositions according to the present invention may instead or in addition to the inorganic peroxygen oxidising agent(s), comprise one or more preformed organic peroxyacid oxidising agents.

Suitable organic peroxyacid oxidising agents for use in the coloring compositions according to the present invention have the general formula:

R - C (O) OOH

wherein R is selected from saturated or unsaturated, substituted or unsubstituted, straight or branched chain, alkyl, aryl or alkaryl groups with from 1 to 14 carbon atoms.

A class of organic peroxyacid compounds suitable for use herein are the amide substituted compounds of the following general formulae:



wherein R^1 is, a saturated or unsaturated alkyl or alkaryl group, or an aryl group, having from 1 to 14 carbon atoms, R^2 is, a saturated or unsaturated alkyl or alkaryl group, or an aryl group, having from 1 to 14 carbon atoms, and R^5 is H or, a saturated or unsaturated alkyl or alkaryl group, or an aryl group, having from 1 to 10 carbon atoms. Amide substituted organic peroxyacid compounds of this type are described in EP-A-0,170,386.

Other suitable organic peroxyacid oxidising agents include peracetic, pernanoic, nonylamidoperoxycaproic acid (NAPCA), perbenzoic, m-chloroperbenzoic, di-peroxy-isophthalic, mono-peroxyphthalic, peroxylauric, hexanesulphonyl peroxy propionic, N,N-phthaloylamino peroxycaproic, monoper succinic, nonanoyloxybenzoic, dodecanedioyl-monoperoxybenzoic, nonylamide of peroxyadipic acid, diacyl and tetraacylperoxides, especially diperoxydodecanedioic acid, diperoxytetradecanedioic acid and diperoxyhexadecanedioic acid and derivatives thereof. Mono- and diperazelaic acid,

mono- and diperbrassylic acid and N-phthaloylaminoperoxicaproic acid and derivatives thereof are also suitable for use herein.

The preformed organic peroxyacid oxidising agents should be safe and effective for use in the compositions herein. Preferably, the preformed organic peroxyacid oxidising agents suitable for use herein will be soluble in the compositions according to the present invention when in liquid form and in the form intended to be used. Preferably, organic peroxyacid oxidising agents suitable for use herein will be water-soluble. Water-soluble preformed organic peroxyacid oxidising agents as defined herein means agents which have a solubility to the extent of about 10g in 1000ml of deionised water at 25°C ("Chemistry" C. E. Mortimer. 5th Edn. p277).

The preferred peroxyacid materials suitable for use herein are selected from peracetic and pernanoic acids and mixtures thereof.

The preformed organic peroxyacid oxidising agent, where present, is preferably present at a level of from about 0.01% to about 8%, more preferably from about 0.1% to about 6%, most preferably from about 0.2% to about 4%, and especially from about 0.3% to about 3% by weight of the hair coloring composition.

When both an inorganic peroxygen oxidising agent and a preformed organic peroxy acid are present in the compositions herein, the weight ratio of the inorganic peroxygen oxidising agent to the preformed organic peroxy acid is preferably in the range of from about 0.0125:1 to about 500:1, more preferably from about 0.0125:1 to about 50:1.

In addition to the inorganic peroxygen oxidising agents and the preformed organic peroxyacid oxidising agents suitable for use herein, the compositions according to the present invention may optionally comprise additional organic peroxides such as urea peroxide, melamine peroxide and mixtures thereof. The level of organic peroxide, where present, is from about 0.01% to about 3%, preferably from about 0.01% to about 2%, more preferably from about 0.1% to about 1.5% and most preferably from about 0.2% to about 1% by weight of composition.

Hair Coloring Agents

The hair coloring compositions of the present invention include as an essential feature an oxidative or non-oxidative hair coloring agent. Such hair coloring agents are used in combination with the oxidising agent and ammonium carbonate and/or ammonium carbamate to formulate permanent, demi-permanent, semi-permanent or temporary hair dye compositions.

Permanent hair dye compositions as defined herein are compositions which once applied to the hair are substantially resistant to wash-out. Demi-permanent hair dye compositions as defined herein are compositions which are substantially removed from the hair after up to 24 washes. Semi-permanent hair dye compositions as defined herein are compositions which once applied to the hair are substantially removed from the hair after up to 10 washes. Temporary hair dye compositions as defined herein are compositions which once applied to the hair are substantially removed from the hair after up to 2 washes. These different types of hair coloring compositions can be formulated via the specific combination of oxidant and/or dyes at different levels and ratios. Wash out as defined herein is the process by which hair color is removed from the hair over time during normal hair cleansing regimen. Washfastness as defined herein, means, the resistance of the dyed hair to wash out.

Oxidative hair coloring agents

A preferred hair coloring agent herein is an oxidative hair coloring agent. The concentration of each oxidative hair coloring agent in the coloring compositions according to the present invention is preferably from about 0.001% to about 3% by weight, more preferably from about 0.01% to about 2% by weight.

The total combined level of oxidative hair coloring agents in the compositions according to the present invention is from about 0.001% to about 5%, preferably from about 0.01% to about 4%, more preferably from about 0.1% to about 3%, most preferably from about 0.1% to about 1% by weight.

Any oxidative hair coloring agent can be used in the compositions according to the present invention. Typically, but without intending to be limited thereby, oxidative hair coloring agents, consist essentially of at least two components, which are collectively referred to as dye forming intermediates (or precursors). Dye forming intermediates can react in the presence of a suitable oxidant to form a colored molecule.

The dye forming intermediates used in oxidative hair colorants include: aromatic diamines, aminophenols, various heterocycles, phenols, napthols and their various derivatives. These dye forming intermediates can be broadly classified as; primary intermediates and secondary intermediates. Primary intermediates, which are also known as oxidative dye precursors, are chemical compounds which become activated upon oxidation and can then react with each other and/or with couplers to form colored dye complexes. The secondary intermediates, also known as color modifiers or couplers, are generally colorless molecules which can form colors in the presence of activated precursors/primary intermediates, and are used with other intermediates to generate specific color effects or to stabilise the color.

Primary intermediates suitable for use in the compositions and processes herein include: aromatic diamines, polyhydric phenols, amino phenols and derivatives of these aromatic compounds (e.g., N-substituted derivatives of the amines, and ethers of the phenols). Such primary intermediates are generally colorless molecules prior to oxidation.

While not wishing to be bound by any particular theory it is proposed herein that the process by which color is generated from these primary intermediates and secondary coupler compounds generally includes a stepwise sequence whereby the primary intermediate can become activated (by oxidation), and then enjoins with a coupler to give a dimeric, conjugated colored species, which in turn can enjoin with another 'activated' primary intermediate to produce a trimeric conjugated colored molecule.

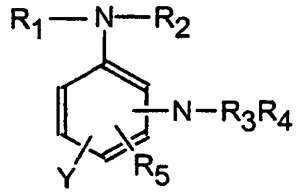
Oxidative Dye Precursors

In general terms, oxidative dye primary intermediates include those monomeric materials which, on oxidation, form oligomers or polymers having extended conjugated systems of electrons in their molecular structure. Because of the new electronic structure, the resultant oligomers and polymers exhibit a shift in their electronic spectra to the visible range and appear colored. For example, oxidative primary intermediates capable of forming colored polymers include materials such as aniline, which has a single functional group and which, on oxidation, forms a series of conjugated imines and quinoid dimers, trimers, etc. ranging in color from green to black. Compounds such as p-phenylenediamine, which has two functional groups, are capable of oxidative polymerization to yield higher molecular weight colored materials having extended

conjugated electron systems. Oxidative dyes known in the art can be used in the compositions according to the present invention. A representative list of primary intermediates and secondary couplers suitable for use herein is found in Sagarin, "Cosmetic Science and Technology"," Interscience, Special Ed. Vol. 2 pages 308 to 310. It is to be understood that the primary intermediates detailed below are only by way of example and are not intended to limit the compositions and processes herein.

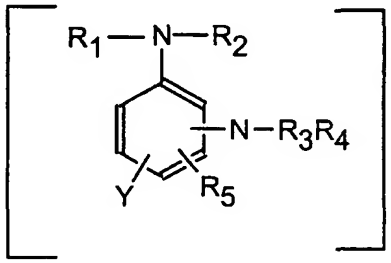
The typical aromatic diamines, polyhydric phenols, amino phenols, and derivatives thereof, described above as primary intermediates can also have additional substituents on the aromatic ring, e.g. halogen, aldehyde, carboxylic acid, nitro, sulfonic acid and substituted and unsubstituted hydrocarbon groups, as well as additional substituents on the amino nitrogen and on the phenolic oxygen, e.g. substituted and unsubstituted alkyl and aryl groups.

Examples of suitable aromatic diamines, amino phenols, polyhydric phenols and derivatives thereof, respectively, are compounds having the general formulas (I), (II) and (III) below:



(I)

OR



HX

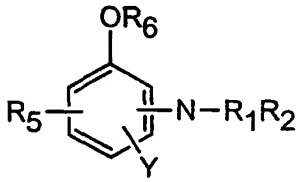
wherein Y is hydrogen, halogen, (e.g. fluorine, chlorine, bromine or iodine), nitro, amino, hydroxyl,

-COOM or -SO_3M (where M is hydrogen or an alkali or alkaline earth metal, ammonium, or substituted ammonium wherein one or more hydrogens on the ammonium ion is replaced with a 1 to 3 carbon atom alkyl or hydroxyalkyl radical), wherein R_1, R_2, R_3 and R_4 are the same or different from each other and are selected from the group consisting of hydrogen, C_1 to C_4 alkyl or alkenyl and C_6 to C_9 aryl, alkaryl or aralkyl, and R_5 is hydrogen, C_1 to C_4 unsubstituted or substituted alkyl or alkenyl wherein the substituents are selected from those designated as Y, above, or C_6 to C_9 unsubstituted or substituted aryl, alkaryl or aralkyl wherein the substituents are selected from those defined as Y, above. Since the precursors of formula (I) are amines, they can be used herein in the form of peroxide-compatible salts, as noted, wherein X represents peroxide-compatible anions of the type herein before detailed. The general formula of the salt indicated is to be understood to encompass those salts having mono-, di-, and tri-negative anions.

Specific examples of formula (I) compounds are: o-phenylenediamine, m-phenylenediamine, p-phenylenediamine, 2-chloro-p-phenylenediamine, 2-iodo-p-phenylenediamine, 4-nitro-o-phenylenediamine, 2-nitro-p-phenylenediamine, 1,3,5-triaminobenzene, 2-hydroxy-p-phenylenediamine, 2,4-diaminobenzoic acid, sodium 2,4-diaminobenzoate, calcium di-2,4-diaminobenzoate, ammonium 2,4-diaminobenzoate, trimethylammonium 2,4-, diaminobenzoate, tri-(2-hydroxyethyl)ammonium 2,4-diaminobenzoate, 2,4-diaminobenzaldehyde carbonate, 2,4-diaminobenzensulfonic acid, potassium 2,4-diaminobenzenesulfonate, N,N-diisopropyl-p-, phenylenediamine bicarbonate, N,N-dimethyl-p-phenylenediamine, N-ethyl-N'-(2-propenyl)-p-phenylenediamine, N-phenyl-p-phenylenediamine, N-phenyl-N-benzyl-p-phenylenediamine, N-ethyl-N'-(3-ethylphenyl)-p-phenylenediamine, 2,4-toluenediamine, 2-ethyl-p-phenylenediamine, 2-(2-bromoethyl)-p-phenylenediamine, 2-phenyl-p-phenylenediamine laurate, 4-(2,5-diaminophenyl)benzaldehyde, 2-benzyl-p-phenylenediamine acetate, 2-(4-nitrobenzyl)-p-phenylenediamine, 2-(4-methylphenyl)-p-phenylenediamine, 2-(2,5-diaminophenyl)-5-methylbenzoic acid,

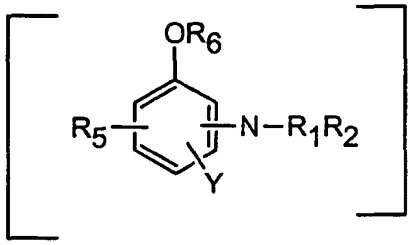
methoxyparaphenylenediamine, dimethyl-p-phenylenediamine, 2,5-dimethylpara-phenylenediamine, 2-methyl-5-methoxy-para-phenylenediamine, 2,6-methyl-5-methoxy-para-phenylenediamine, 3-methyl-4-amino-N,N-diethylaniline, N,N-bis(β-hydroxyethyl)-para-phenylenediamine, 3-methyl-4-amino-N,N-bis(β-hydroxyethyl)aniline, 3-chloro-4-amino-N,N-bis(β-hydroxyethyl)aniline, 4-amino-N-ethyl-N-(carbamethyl)aniline, 3-methyl-4-amino-N-ethyl-N-(carbamethyl)aniline, 4-amino-N-ethyl-(β-piperidonoethyl)aniline, 3-methyl-4-amino-N-ethyl-(β-piperidonoethyl)aniline, 4-amino-N-ethyl-N-(β-morpholinoethyl)aniline, 3-methyl-4-amino-N-ethyl-N-(β-morpholinoethyl)aniline, 4-amino-N-ethyl-N-(β-acetylaminoethyl)aniline, 4-amino-N-(β-methoxyethyl) aniline, 3-methyl-4-amino-N-ethyl-N-(β-acetylaminoethyl) aniline, 4-amino-N-ethyl-N-(β-mesylaminoethyl) aniline, 3-methyl-4-amino-N-ethyl-N-(β-mesylaminoethyl) aniline, 4-amino-N-ethyl-N-(β-sulphoethyl) aniline, 3-methyl-4-amino-N-ethyl-N-(β-sulphoethyl) aniline, N-(4-aminophenyl)morpholine, N-(4-aminophenyl)piperidine, 2,3-dimethyl-p-phenylenediamine, isopropyl-p-phenylenediamine, N,N-bis-(2-hydroxyethyl)-p-phenylenediamine sulphate.

Compounds having the general structure (II) are as follows:



(II)

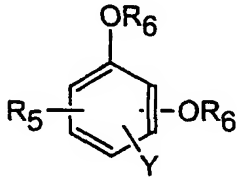
OR



HX

where X and Y are the same as in formula (I), R_1 and R_2 can be the same or different from each other and are the same as in formula (I), R_5 is the same as in formula (I) and R_6 is hydrogen or C_1 to C_4 substituted or unsubstituted alkyl or alkenyl wherein the substituents are selected from those defined as Y in formula (I).

Specific examples of formula (II) compounds are:
o-aminophenol, m-aminophenol, p-aminophenol, 2-iodo-p-aminophenol, 2-nitro-p-aminophenol, 3,4-dihydroxyaniline, 3,4-diaminophenol, chloroacetate, 2-hydroxy-4-aminobenzoic acid, 2-hydroxy-4-aminobenzaldehyde, 3-amino-4-hydroxybenzenesulfonic acid, N,N-diisopropyl-p-aminophenol, N-methyl-N-(1-propenyl)-p-aminophenol, N-phenyl-N-benzyl-p-aminophenol sulphate, N-methyl-N-(3-ethylphenyl)-p-aminophenol, 2-nitro-5-ethyl-p-aminophenol, 2-nitro-5-(2-bromoethyl)-p-aminophenol, (2-hydroxy-5-aminophenyl)acetaldehyde, 2-methyl-p-aminophenol, (2-hydroxy-5-aminophenyl)acetic acid, 3-(2-hydroxy-5-aminophenyl)-1-propene, 3-(2-hydroxy-5-aminophenyl)-2-chloro-1-propene, 2-phenyl-p-aminophenol palmitate, 2-(4-nitrophenyl)-p-aminophenol, 2-benzyl-p-aminophenol, 2-(4-chlorobenzyl-p-aminophenol perchlorate, 2-(4-methylphenyl)-p-aminophenol, 2-(2-amino-4-methylphenyl)-p-aminophenol, p-methoxyaniline, 2-bromoethyl-4-aminophenyl ether phosphate, 2-nitroethyl-4-aminophenyl ether bromide, 2-aminoethyl-4-aminophenyl ether , 2-hydroxyethyl-4-aminophenyl ether, (4-aminophenoxy)acetaldehyde, (4-aminophenoxy)acetic acid, (4-aminophenoxy)methanesulfonic acid, 1-propenyl-4-aminophenyl ether isobutyrate, (2-chloro)-1-propenyl-4-aminophenyl ether, (2-nitro)-1-propenyl-4-aminophenyl ether, (2-amino)-propenyl-4-aminophenyl ether, (2-hydroxy)-1-propenyl-4-aminophenyl ether, N-methyl-p-aminophenol, 3-methyl-4-aminophenol, 2-chloro-4-aminophenol, 3-chloro-4-aminophenol, 2,6-dimethyl-4-aminophenol, 3,5-dimethyl-4-aminophenol, 2,3-dimethyl-4-aminophenol, 2,5-dimethyl-4-aminophenol, 2-hydroxymethyl-4-aminophenol, 3-hydroxymethyl-4-aminophenol, 2,6-dichloro-4-aminophenol, 2,6-dibromo-4-aminophenol and 2-bromo-4-aminophenol.



(III)

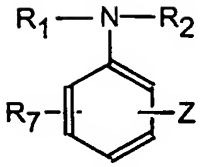
Specific examples of formula (III) compounds are:
o-hydroxyphenol (catechol), m-hydroxyphenol (resorcinol), p-hydroxyphenol (hydroquinone), 4-methoxyphenol, 2-methoxyphenol, 4-(2-chloroethoxy) phenol, 4-(2-propenoxy) phenol, 4-(3-chloro-2-propenoxy) phenol, 2-chloro-4-hydroxyphenol (2-chlorohydroquinone), 2-nitro-4-hydroxyphenol(2-nitrohydroquinone), 2-amino-4-

hydroxyphenol, 1,2,3-trihydroxybenzene (pyrogallol), 2,4-dihydroxybenzaldehyde, 3,4-dihydoxybenzoic acid, 2,4-dihydroxybenzenesulfonic acid, 3-ethyl-4-hydroxyphenol, 3-(2-nitroethyl)-4-hydroxyphenol, 3-(2-propenyl)-4-hydroxyphenol, 3-(3-chloro-2-propenyl)-4-hydroxyphenol, 2-phenyl-4-hydroxyphenol, 2-(4-chlorophenyl)-4-hydroxyphenol, 2-benzyl-4-hydroxyphenol, 2-(2-nitrophenyl)-4-hydroxyphenol, 2-(2-methylphenyl)-4-hydroxyphenol, 2-(2-methyl-4-chlorophenyl)-4-hydroxyphenol, 3-methoxy-4-hydroxy-benzaldehyde, 2-methoxy-4-(1-propenyl)phenol, 4-hydroxy-3-methoxycinnamic acid, 2,5-dimethoxyaniline, 2-methylresorcinol, alpha napthol and salts thereof.

Secondary coupling compounds which are suitable for inclusion in the coloring compositions and processes herein before described include certain aromatic amines and phenols and derivatives thereof which do not produce color singly, but which modify the color, shade or intensity of the colors developed by the primary oxidized dye intermediates. Certain aromatic amines and phenolic compounds, and derivatives thereof, including some aromatic diamines and polyhydric phenols of the types described by formulas (I), (Ia), (Ib), (II) and (III) above, but which are well known in the art not to be suitable primary intermediates, are suitable as couplers herein. Polyhydric alcohols are also suitable for use as couplers herein.

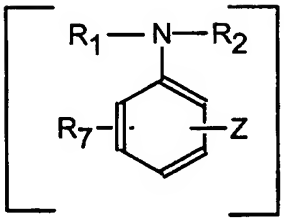
The aromatic amines and phenols and derivatives described above as couplers can also have additional substituents on the aromatic ring, e.g., halogen, aldehyde, carboxylic acid, nitro, sulfonyl and substituted and unsubstituted by hydrocarbon groups, as well as additional substituents on the amino nitrogen, or phenolic oxygen, e.g. substituted and unsubstituted alkyl and aryl groups. Again, peroxide-compatible salts thereof are suitable for use herein.

Examples of aromatic amines, phenols and derivatives thereof are compounds of the general formulas (IV) and (V) below:



(IV)

OR



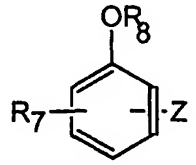
HX

wherein Z is hydrogen, C_1 and C_3 alkyl, halogen (e.g. fluorine, chlorine, bromine or iodine) nitro,

-COOM or SO_3M, (where M is hydrogen or an alkali or alkaline earth metal, ammonium or substituted ammonium wherein one or more hydrogens on the ammonium ion is replaced with a 1 to 3 carbon atom alkyl or hydroxyalkyl radical), wherein R_1 and R_2 are the same or different and are selected from the group consisting of hydrogen, C_1 to C_4 alkyl or alkenyl and C_6 to C_9 aryl, alkaryl or aralkyl and R_7 is hydrogen, C_1 to C_4 unsubstituted or substituted alkyl or alkenyl wherein the substituents are selected from those designated as Z above or C_6 to C_9 unsubstituted or substituted aryl, alkaryl or aralkyl wherein the substituents are selected from those defined as Z above and wherein X is as defined in formula (I).

Specific examples of formula (IV) compounds are:
aniline, p-chloroaniline, p-fluoroaniline, p-nitroaniline, p-aminobenzaldehyde, p-aminobenzoic acid, sodium-p-aminobenzoate, lithium-p-aminobenzoate, calcium di-p-aminobenzoate, ammonium-p-aminobenzoate, trimethylammonium-p-aminobenzoate, tri(2-hydroxyethyl)-p-aminobenzoate, p-aminobenzenesulfonic acid, potassium p-aminobenzenesulfonate, N-methylaniline, N-propyl-N-phenylaniline, N-methyl-N-2-propenylaniline, N-benzylaniline, N-(2-ethylphenyl)aniline, 4-methylaniline, 4-(2-bromoethyl)aniline, 2-(2-nitroethyl)aniline, (4-aminophenyl)acetaldehyde, (4-

aminophenyl)acetic acid, 4-(2-propenyl)aniline acetate, 4-(3-bromo-2-propenyl)aniline, 4-phenylaniline chloroacetate, 4-(3-chlorophenyl)aniline, 4-benzylaniline, 4-(4-iodobenzyl)aniline, 4-(3-ethylphenyl)aniline, 4-(2-chloro-4-ethylphenyl)aniline.



(V)

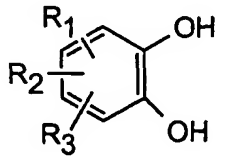
wherein Z and R_7 are defined as in formula (IV) and R_8 is hydrogen or C_1 to C_4 substituted or unsubstituted alkyl or alkenyl wherein the substituents are selected from those defined as Z in formula (IV).

Specific examples of formula (V) compounds are:
phenol, p-chlorophenol, p-nitrophenol, p-hydroxybenzaldehyde, p-hydroxybenzoic acid, p-hydroxybenzenesulfonic acid, ethylphenyl ether, 2-chloroethylphenyl ether, 2-nitroethylphenyl ether, phenoxyacetaldehyde, phenoxyacetic acid, 3-phenoxy-1-propene, 3-phenoxy-2-nitro-1-propene, 3-phenoxy-2-bromo-1-propene, 4-propylphenol, 4-(3-bromopropyl)phenol, 2-(2-nitroethyl)phenol, (4-hydroxyphenyl)acetaldehyde, (4-hydroxyphenyl)acetic acid, 4-(2-propenyl)phenol, 4-phenylphenol, 4-benzylphenol, 4-(3-fluoro-2-propenyl)phenol, 4-(4-chlorobenzyl)phenol, 4-(3-ethylphenyl)phenol, 4-(2-chloro-3-ethylphenyl)phenol, 2,5-xylenol, 2,5-diaminopyridine, 2-hydroxy-5-aminopyridine, 2-amino-3-hydroxy pyridine, tetraaminopyrimindine, 1,2,4-trihydroxybenzene, 1,2,4-trihydroxy-5-(C_1-C_6-alkyl)benzene, 1,2,3-trihydroxybenzene, 4-aminoresorcinol, 1,2-dihydroxybenzene, 2-amino-1,4-dihydroxybenzene, 2-amino-4-methoxy-phenol, 2,4-diaminophenol, 3-methoxy-1,2-dihydroxy-benzene, 1,4-dihydroxy-2-(N,N-diethylamino)benzene, 2,5-diamino-4-methoxy-1-hydroxybenzene, 4,6-dimethoxy-3-amino-1-hydroxybenzene, 2,6-dimethyl-4-[N-(p-hydroxyphenyl)amino]-1-hydroxybenzene, 1,5-diamino-2-methyl-4-[N-(p-hydroxyphenyl)amino]benzene and salts thereof.

Additional primary intermediates suitable for use herein include catechol species and in particular catechol "dopa" species which includes dopa itself as well as homologs, analogs and derivatives of DOPA. Examples of suitable cachetol species include cysteinyl dopa, alpha alkyl dopa having 1 to 4 , preferably 1 to 2 carbon atoms in the

alkyl group, epinephrine and dopa alkyl esters having 1 to 6 , preferably 1 to 2 carbon atoms in the alkyl group.

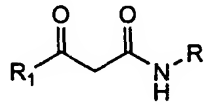
In general suitable catechols are represented by formula (VI) below:



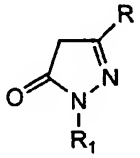
(VI)

wherein R_1, R_2 and R_3, which may be the same or different, are electron donor or acceptor substutuents selected from H, lower (C_1-C_6) alkyl, OH, OR, COOR, NHCOR, CN, COOH, Halogen, NO_2, CF_3, SO_3H or NR_4R_5, with the proviso that only one of the R_1, R_2 or R_3 can be CN, COOH, halogen, NO_2, CF_3 or SO_3H: R_4 and R_5, which may be the same or different, are H, lower (C_1-C_6) alkyl or substituted lower (C_1-C_6) alkyl in which the substituent may be OH, OR, $NHCOR_6$, $NHCONH_2$, $NHCO_2R_6$, $NHCSNH_2$, CN, COOH, SO_3H, SO_2NR_6, SO_2R_6 or CO_2R_6; R_6 is lower (C_1-C_6) alkyl, lower (C_1-C_6) hydroxyalkyl phenyl linked to the nitrogen by an alkylene chain, phenyl or substituted phenyl with the substituent defined as R_1, and R is C_1-C_6 alkyl or C_1-C_6 hydroxyalkyl.

Also included herein are oxidative hair coloring agents of the formula:



wherein: R_1 = substituted or unsubstituted benzene ring, tertiary-butyl, etc.; R = substituted or unsubstituted benzene ring and the formula:



wherein R = aminoalkyl, amidoalkyl, aminobenzene (substituted or unsubstituted), amidobenzene (substituted or unsubstituted), alkyl, substituted or unsubstituted benzene ring ; R_1 = substituted or unsubstituted benzene ring.

The primary intermediates can be used herein alone or in combination with other primary intermediates, and one or more can be used in combination with one or more couplers. The choice of primary intermediates and couplers will be determined by the color, shade and intensity of coloration which is desired. There are nineteen preferred primary intermediates and couplers which can be used herein, singly or in combination, to provide dyes having a variety of shades ranging from ash blonde to black; these are: pyrogallol, resorcinol, p-toluenediamine, p-phenylenediamine, o-phenylenediamine, m-phenylenediamine, o-aminophenol, p-aminophenol, 4-amino-2-nitrophenol, nitro-p-phenylenediamine, N-phenyl-p-phenylenediamine, m-aminophenol, 2-amino-3-hydroxypyridine, 1-napthol, N,N bis (2-hydroxyethyl)p-phenylenediamine, 4-amino-2-hydroxytoluene, 1,5-dihydroxynapthalene, 2-methyl resorcinol and 2,4-diaminoanisole. These can be used in the molecular form or in the form of peroxide-compatible salts, as detailed above.

For example low intensity colors such as natural blond to light brown hair shades generally comprise from about 0.001% to about 5%, preferably from about 0.1% to about 2%, more preferably from about 0.2% to about 1% by weight of coloring composition of total oxidative dyeing agents and may be achieved by the combination of primary intermediates such as 1,4-diamino-benzene, 2,5-diamino toluene, 2,5-diamino-anisole, 4-aminophenol, 2,5-diamino-benzyl alcohol and 2-(2',5'-diamino)phenyl-ethanol with couplers such as resorcinol, 2-methyl resorcinol or 4-chloro resorcinol.

Similarly combination of the above primary intermediates with couplers, such as, 5-amino-2-methyl phenol and 1,3-diamino-benzene derivatives such as 2,4-diamino-anisole at levels of from about 0.5% to about 1% of total dyeing agents can lead to medium intensity red colors. High intensity colors such as blue to blue-violet hair shades can be produced by the combination of the above primary intermediates with couplers such as 1,3-diamino-benzene or its derivatives such as 2,5-diamino-toluene at levels of from about 1% to about 6% by weight of composition of total dyeing agents. Black hair colors can be obtained by combining the aforementioned primary intermediates with couplers such as 1,3-diaminobenzene or its derivatives

Non-oxidative and other dyes

The hair coloring compositions of the present invention may, in addition to or instead of an oxidative hair coloring agent, include non-oxidative and other dye materials. Optional non-oxidative and other dyes suitable for use in the hair coloring compositions and processes according to the present invention include both semi-permanent, temporary and other dyes. Non-oxidative dyes as defined herein include the so-called 'direct action dyes', metallic dyes, metal chelate dyes, fibre reactive dyes and other synthetic and natural dyes. Various types of non-oxidative dyes are detailed in: 'Chemical and Physical Behaviour of Human Hair' 3rd Ed. by Clarence Robbins (pp250-259); 'The Chemistry and Manufacture of Cosmetics'. Volume IV. 2nd Ed. Maison G. De Navarre at chapter 45 by G.S. Kass (pp841-920); 'cosmetics: Science and Technology' 2nd Ed., Vol. II Balsam Sagarin, Chapter 23 by F.E. Wall (pp 279-343); 'The Science of Hair Care' edited by C. Zviak, Chapter 7 (pp 235-261) and .'Hair Dyes', J.C. Johnson, Noyes Data Corp., Park Ridge, U.S.A. (1973), (pp 3-91 and 113-139).

Direct action dyes which do not require an oxidative effect in order to develop the color, are also designated hair tints and have long been known in the art. They are usually applied to the hair in a base matrix which includes surfactant material. Direct action dyes include nitro dyes such as the derivatives of nitroamino benzene or nitroaminophenol; disperse dyes such as nitroaryl amines, aminoanthraquinones or azo dyes; anthraquinone dyes, naphthoquinone dyes; basic dyes such as Acridine Orange C.I. 46005.

Nitrodyes are added to dyeing compositions to enhance colour of colorant and to add suitable aesthetic colour to the dye mixture prior to application.

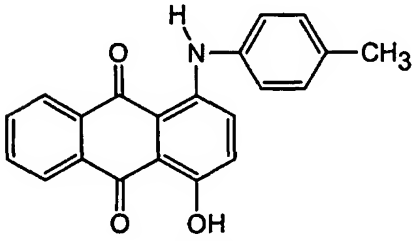
Further examples of direct action dyes include the Arianor dyes basic brown 17, C.I.(color index) - no. 12,251; basic red 76, C.I. - 12,245; basic brown 16, C.I. - 12,250; basic yellow 57, C.I. - 12,719 and basic blue 99, C.I. - 56,059 and further direct action dyes such as acid yellow 1, C.I. - 10,316 (D&C yellow no.7); acid yellow 9, C.I. - 13,015; basic violet C.I. - 45,170; disperse yellow 3, C.I. - 11,855; basic yellow 57, C.I. - 12,719; disperse yellow 1, C.I. - 10,345; basic violet 1, C.I. - 42,535, basic violet 3, C.I. - 42,555; greenish blue, C.I. - 42090 (FD&C Blue no.1); yellowish red, C.I.-14700 (FD&C red no.4); yellow, C.I.19140 (FD&C yellow no5); yellowish orange, C.I.15985 (FD&C yellow no.6); bluish green, C.I.42053 (FD&C green no.3); yellowish red, C.I.16035 (FD&C red no.40); bluish green, C.I.61570 (D&C green no.3); orange, C.I.45370 (D&C orange no.5); red, C.I.15850 (D&C red no.6); bluish red, C.I.15850(D&C red no.7); slight

bluish red, C.I.45380(D&C red no.22); bluish red, C.I.45410(D&C red no.28); bluish red, C.I.73360(D&C red no.30); reddish purple, C.I.17200(D&C red no.33); dirty blue red, C.I.15880(D&C red no.34); bright yellow red, C.I.12085(D&C red no.36); bright orange, C.I.15510(D&C orange no.4); greenish yellow, C.I.47005(D&C yellow no.10); bluish green, C.I.59040(D&C green no.8); bluish violet, C.I.60730(Ext. D&C violet no.2); greenish yellow, C.I.10316(Ext. D&C yellow no.7);

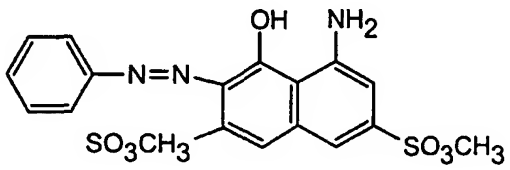
Fibre reactive dyes include the Procion (RTM), Drimarene (RTM), Cibacron (RTM), Levafix (RTM) and Remazol (RTM) dyes available from ICI, Sandoz, Ciba-Geigy, Bayer and Hoechst respectively.

Natural dyes and vegetable dyes as defined herein include henna *(Lawsonia alba)*, camomile *(Matricaria chamomila or Anthemis nobilis)*, indigo, logwood and walnut hull extract.

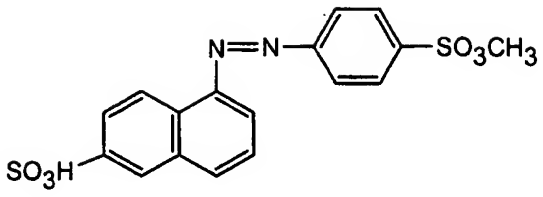
Temporary hair dyes, or hair coloring rinses, are generally comprised of dye molecules which are too large to diffuse into the hair shaft and which act on the exterior of the hair. They are usually applied via a leave-in procedure in which the dye solution is allowed to dry on the hair surface. As such these dyes are typically less resistant to the effects of washing and cleaning the hair with surface active agents and are washed off of the hair with relative ease. Any temporary hair dye may suitably be used in the compositions of the invention and examples of preferred temporary hair dyes are illustrated below.



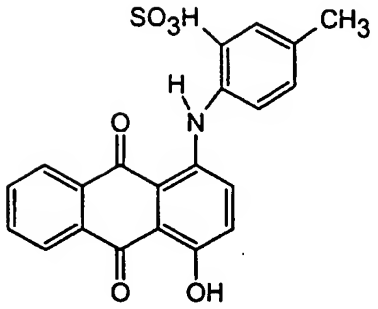
Violet



Red

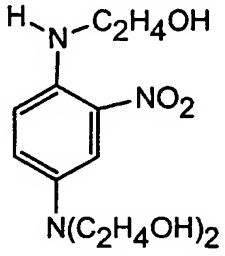


Yellow

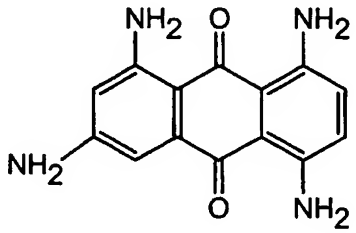


Blue-Violet

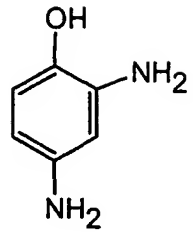
Semi-permanent hair dyes are dyes which are generally smaller in size and effect to temporary hair rinses but are generally larger than permanent (oxidative) dyes. Typically, semi-permanent dyes act in a similar manner to oxidative dyes in that they have the potential to diffuse into the hair shaft. However, semi-permanent dyes are generally smaller in size than the aforementioned conjugated oxidative dye molecules and as such are pre-disposed to gradual diffusion out of the hair again. Simple hair washing and cleaning action will encourage this process and in general semi-permanent dyes are largely washed out of the hair after about 5 to 8 washes. Any semi-permanent dye system may be suitably used in the compositions of the present invention. Suitable semi-permanent dyes for use in the compositions of the present invention are HC Blue 2, HC Yellow 4, HC Red 3, Disperse Violet 4, Disperse Black 9, HC Blue 7, HC Yellow 2, Disperse Blue 3, Disperse violet 1 and mixtures thereof. Examples of semi-permanent dyes are illustrated below:



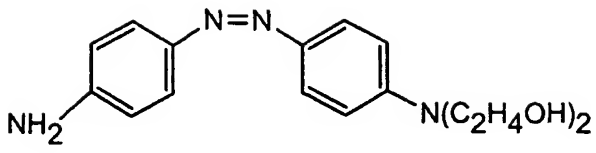
Blue



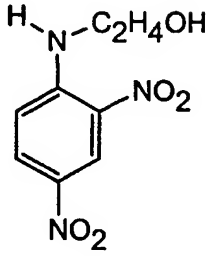
Blue



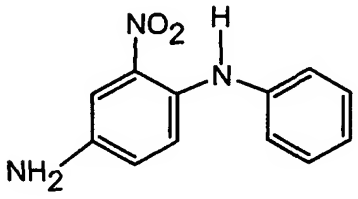
Yellow



Yellow



Red



Red

Typical semi-permanent dye systems incorporate mixtures of both large and small color molecules. As the size of the hair is not uniform from root to tip the small molecules will diffuse both at the root and tip, but will not be retained within the tip, while the larger molecules will be generally only be able to diffuse into the ends of the hair. This combination of dye molecule size is used to help give consistent color results from the root to the tip of the hair both during the initial dyeing process and during subsequent washing.

Ammonium carbonate and/or carbamate

Another essential component of the compositions herein is ammonium carbonate and/or ammonium carbamate, preferably at a level of from about 0.01% to about 10%, more preferably from about 0.1% to about 5%, and especially from about 2% to about 5% by weight.

The coloring compositions of the present invention have a pH in the range of from about 7 to about 9 , preferably from about 8 to about 9.

The pH of the preferred coloring compositions of the present invention are maintained within the desired pH range via the action of the inorganic peroxygen oxidising agent and the ammonium carbonate and/or ammonium carbamate. However, if so desired, the compositions may contain one or more optional buffering agents and/or hair swelling agents (HSAs). Several different pH modifiers can be used to adjust the pH of the final composition or any constituent part thereof. However, preferred compositions herein are substantially free of additional buffering agents, buffering agents and hair swelling agents, i.e. they comprise less than about 1%, preferably less than about 0.5%, more preferably less than about 0.1% by weight of such agents.

This pH adjustment can be effected by using well known acidifying agents in the field of treating keratinous fibres, and in particular human hair, such as inorganic and organic acids such as hydrochloric acid, tartaric acid, citric acid, succinic acid, phosphoric acid and carboxylic or sulphonic acids such as ascorbic acid, acetic acid, lactic acid, sulphuric acid, formic acid, ammonium sulphate and sodium dihydrogenphosphate /phosphoric acid, disodium hydrogenphosphate /phosphoric acid, potassium chloride /hydrochloric acid, potassium dihydrogen phthalate/ hydrochloric acid, sodium citrate / hydrochloric acid, potassium dihydrogen citrate /hydrochloric acid, potassium dihydrogencitrate/ citric acid, sodium citrate / citric acid, sodium tartarate/ tartaric acid, sodium lactate/ lactic acid, sodium acetate/ acetic acid, disodium hydrogenphosphate/ citric acid and sodium chloride/ glycine / hydrochloric acid, succinic acid and mixtures thereof.

Examples of alkaline buffering agents are ammonium hydroxide, ethylamine, dipropylamine, triethylamine and alkanediamines such as 1,3-diaminopropane, anhydrous alkaline alkanolamines such as, mono or di- ethanolamine, preferably those which are completely substituted on the amine group such as dimethylaminoethanol, polyalkylene polyamines such as diethylenetriamine or a heterocyclic amine such as morpholine as well as the hydroxides of alkali metals, such as sodium and potassium hydroxide, hydroxides of alkali earth metals, such as magnesium and calcium hydroxide, basic amino acids such as L-argenine, lysine, alanine, leucine, iso-leucine, oxylysine and histidine and alkanolamines such as dimethylaminoethanol and aminoalkylpropanediol and mixtures thereof. Also suitable for use herein are compounds other than ammonium carbonate or ammonium carbamate that form HCO_3^- by dissociation in water (hereinafter referred to as 'ion forming compounds'). Examples of suitable ion forming compounds are Na_2CO_3, $NaHCO_3$, K_2CO_3, NH_4HCO_3, $CaCO_3$ and $Ca(HCO_3)$ and mixtures thereof.

The bleaching and coloring compositions according to the present invention, may, as will be described later herein, be comprised of a final solution containing oxidising agent, hair coloring agent and ammonium carbonate and/or ammonium carbamate which have been admixed prior to application to the hair or a single component system. As such, the compositions according to the present invention may comprise coloring kits of a number of separate components.

In oxidising and coloring kits comprising a portion of inorganic peroxygen oxidising agent, such as hydrogen peroxide, which may be present in either solid or liquid form, a buffering agent solution can be used to stabilise hydrogen peroxide. Since hydrogen peroxide is stable in the pH range from 2 to 4, it is preferable to use a buffering agent having a pH within this range. Dilute acids are suitable hydrogen peroxide buffering agents.

Catalyst

The coloring compositions herein may optionally contain a transition metal containing catalyst for the inorganic peroxygen oxidising agents and the, optional, preformed peroxy acid oxidising agent(s). One suitable type of catalyst is a catalyst system comprising a heavy metal cation of defined bleach catalytic activity, such as copper, iron or manganese cations, an auxiliary metal cation having little or no bleach catalytic activity, such as zinc or aluminium cations, and a sequestrant having defined stability constants for the catalytic and auxiliary metal cations, particularly ethylenediaminetetraacetic acid, ethylenediaminetetra (methylenephosphonic acid) and water-soluble salts thereof. Such catalysts are disclosed in US-A-4,430,243.

Other types of suitable catalysts include the manganese-based complexes disclosed in US-A-5,246,621 and US-A-5,244,594. Preferred examples of these catalysts include $Mn^{IV}_2(u\text{-}O)_3$(1,4,7-trimethyl-1,4,7-triazacyclononane)$_2$-$(PF_6)_2$, $Mn^{III}_2(u\text{-}O)_1(u\text{-}OAc)_2$(1,4,7-trimethyl-1,4,7-triazacyclononane)$_2$-$(ClO_4)_2$, $Mn^{IV}_4(u\text{-}O)_6$(1,4,7-triazacyclononane)$_4$-$(ClO_4)_2$, $Mn^{III}Mn^{IV}_4(u\text{-}O)_1(u\text{-}OAc)_2$-(1,4,7-trimethyl-1,4,7-triazacyclononane)$_2$-$(ClO_4)_3$, and mixtures thereof. Others are described in EP-A-0,549,272. Other ligands suitable for use herein include 1,5,9-trimethyl-1,5,9-triazacyclododecane, 2-methyl-1,4,7-triazacyclononane, 2-methyl-1,4,7-triazacyclononane, 1,2,4,7-tetramethyl-1,4,7-triazacyclononane, and mixtures thereof.

For examples of suitable catalysts see US-A-4,246,612 and US-A-5,227,084. See also US-A-5,194,416 which teaches mononuclear manganese (IV) complexes such as Mn(1,4,7-trimethyl-1,4,7-triazacyclononane)$(OCH_3)_3$-(PF_6). Still another type of suitably catalyst, as disclosed in US-A-5,114,606, is a water-soluble complex of manganese (III), and/or (IV) with a ligand which is a non-carboxylate polyhydroxy compound having at least three consecutive C-OH groups. Other examples include binuclear Mn complexed with tetra-N-dentate and bi-N-dentate ligands, including $N_4Mn^{III}(u\text{-}O)_2Mn^{IV}N_4)^+$and $[Bipy_2Mn^{III}(u\text{-}O)_2Mn^{IV}bipy_2]$-$(ClO_4)_3$.

Further suitable catalysts are described, for example, in EP-A-0,408,131 (cobalt complex catalysts), EP-A-0,384,503, and EP-A-0,306,089 (metallo-porphyrin catalysts), US-A-4,728,455 (manganese/multidentate ligand catalyst), US-A-4,711,748 and EP-A-0.224,952, (absorbed manganese on aluminosilicate catalyst), US-A-4,601,845 (aluminosilicate support with manganese and zinc or magnesium salt), US-A-4,626,373 (manganese/ligand catalyst), US-A-4,119,557 (ferric complex catalyst), DE-A-2,054,019 (cobalt chelant catalyst) CA-A-866,191 (transition metal-containing salts), US-A-4,430,243 (chelants with manganese cations and non-catalytic metal cations), and US-A-4,728,455 (manganese gluconate catalysts).

Heavy metal ion sequestrant

The coloring compositions of the invention may contain as an optional component a heavy metal ion sequestrant. By heavy metal ion sequestrant it is meant herein components which act to sequester (chelate or scavenge) heavy metal ions. These components may also have calcium and magnesium chelation capacity, but preferentially they show selectivity to binding heavy metal ions such as iron, manganese and copper. Such sequestering agents are valuable in hair coloring compositions as herein described for the delivery of controlled oxidising action as well as for the provision of good storage stability of the hair coloring products.

Heavy metal ion sequestrants are generally present at a level of from about 0.005% to about 20%, preferably from about 0.01% to about 10%, more preferably from about 0.05% to about 2% by weight of the compositions.

Various sequestering agents, including the amino phosphonates, available as Dequest (RTM) from Monsanto, the nitriloacetates, the hydroxyethyl-ethylene triamines and the like are known for such use. Suitable heavy metal ion sequestrants for use herein include organic phosphonates, such as the amino alkylene poly (alkylene phosphonates), alkali metal ethane 1-hydroxy disphosphonates and nitrilo trimethylene phosphonates.

Preferred among the above species are diethylene triamine penta (methylene phosphonate), ethylene diamine tri (methylene phosphonate) hexamethylene diamine tetra (methylene phosphonate) and hydroxy-ethylene 1,1 diphosphonate.

Preferred biodegradable non-phosphorous heavy metal ion sequestrants suitable for use herein include nitrilotriacetic acid and polyaminocarboxylic acids such as ethylenediaminotetracetic acid, ethylenetriamine pentaacetic acid, ethylenediamine disuccinic acid, ethylenediamine diglutaric acid, 2-hydroxypropylenediamine disuccinic acid or any salts thereof. Especially preferred is ethylenediamine-N,N'-disuccinic acid (EDDS). see US-A-4,704,233, or the alkali metal, alkaline earth metal, ammonium, or substituted ammonium salts thereof, or mixtures thereof.

Other suitable heavy metal ion sequestrants for use herein are iminodiacetic acid derivatives such as 2-hydroxyethyl diacetic acid or glyceryl imino diacetic acid, described in EP-A-317,542 and EP-A-399,133. The iminodiacetic acid-N-2-hydroxypropyl sulfonic acid and aspartic acid N-carboxymethyl N-2-hydroxypropyl-3-sulfonic acid sequestrants described in EP-A-516,102 are also suitable herein. The β-alanine-N,N'-diacetic acid, aspartic acid-N,N'-diacetic acid, aspartic acid-N-monoacetic acid and iminodisuccinic acid sequestrants described in EP-A-509,382 are also suitable.

EP-A-476,257 describes suitable amino based sequestrants. EP-A-510,331 describes suitable sequestrants derived from collagen, keratin or casein. EP-A-528,859 describes a suitable alkyl iminodiacetic acid sequestrant. Dipicolinic acid and 2-phosphonobutane-1,2,4-tricarboxylic acid are also suitable. Glycinamide-N,N'-disuccinic acid (GADS), ethylenediamine-N-N'-diglutaric acid (EDDG) and 2-hydroxypropylenediamine-N-N'-disuccinic acid (HPDDS) are also suitable.

The heavy metal ion sequestering agents of the present invention may be used in their alkali or alkaline earth metal salts.

Thickeners

The coloring compositions of the present invention may additionally include a thickener at a level of from about 0.05% to about 20%, preferably from about 0.1% to about 10%, more preferably from about 0.5% to about 5% by weight. Thickening agents suitable for use in the compositions herein are selected from oleic acid, cetyl alcohol, oleyl alcohol, sodium chloride, cetearyl alcohol, stearyl alcohol, synthetic thickeners such as Carbopol, Aculyn and Acrosyl and mixtures thereof. Preferred thickeners for use herein are Aculyn 22 (RTM), steareth-20 methacrylate copolymer; Aculyn 44 (RTM) ,polyurethane resin and Acusol 830 (RTM), acrylates copolymer which are available from Rohm and Haas, Philadelphia, PA, USA. Additional thickening agents suitable for use herein include sodium alginate or gum arabic, or cellulose derivatives, such as methyl cellulose or the sodium salt of carboxymethylcellulose or acrylic polymers.

Diluent

Water is the preferred diluent for the compositions according to the present invention. However, the compositions according to the present invention may include one or more solvents as additional diluent materials. Generally, solvents suitable for use in the coloring compositions of the present invention are selected to be miscible with water and innocuous to the skin. Solvents suitable for use as additional diluents herein include C_1-C_{20} mono- or polyhydric alcohols and their ethers, glycerine, with monohydric and dihydric alcohols and their ethers preferred. In these compounds, alcoholic residues containing 2 to 10 carbon atoms are preferred. Thus, a preferred group includes ethanol, isopropanol, n-propanol, butanol, propylene glycol, ethylene glycol monoethyl ether, and mixtures thereof. Water is the preferred principal diluent in the compositions according to the present invention. Principal diluent, as defined herein, means, that the level of water present is higher than the total level of any other diluents.

The diluent is present at a level preferably of from about 5% to about 99.98%, preferably from about 15% to about 99.5%, more preferably at least from about 30% to about 99%, and especially from about 50% to about 98% by weight of the compositions herein.

Enzyme

A further additional material useful in the hair coloring compositions according to the present invention is one or more enzymes.

Suitable enzymatic materials include the commercially available lipases, cutinases, amylases, neutral and alkaline proteases, esterases, cellulases, pectinases, lactases and peroxidases conventionally incorporated into detergent compositions. Suitable enzymes are discussed in US Patents 3,519,570 and 3,533,139.

Peroxidases are haemoproteins specific for peroxide, but using a wide range of substances as donors. Catalase which decomposes peroxide, is included here in view of the fact that it is generally similar in structure and properties and is able to bring about certain oxidations by H_2O_2. The decomposition of H_2O_2 can be regarded as the oxidation of one molecule by the other. It is widespread in aerobic cells and may have some more important function. The coenzyme peroxidases are not haemoproteins and one at least is a flavoprotein. Other flavoproteins such as xanthine oxidase will also use H_2O_2 among other acceptors, and the coenzyme peroxidases resemble these rather than the classical peroxidases in not being specific for H_2O_2. Suitable peroxidases for the compositions of the present invention include horseradish peroxidase, Japanese radish peroxidase, cow's milk peroxidase, rat liver peroxidase, linginase and haloperoxidase such as chloro- and bromo-peroxidase.

Enzymes are optionally incorporated at levels sufficient to provide up to about 50 mg by weight, more typically about 0.01mg to about 10 mg of active enzyme per gramm of the hair treatment composition of the invention. Stated otherwise the peroxidase enzyme may be incorporated into the compositions in accordance with the invention at a level of from about 0.0001% to about 5%, preferably from about 0.001% to about 1%, more preferably from about 0.01% to about 1% active enzyme by weight of the composition.

Commercially available protease enzymes include those sold under the trade names Alcalase, Savinase, Primase, Durazym, and Esperase by Novo Industries A/S (Denmark), those sold under the tradename Maxatase, Maxacal and Maxapem by Gist-Brocades, those sold by Genencor International, and those sold under the tradename Opticlean and Optimase by Solvay Enzymes. Protease enzyme may be incorporated into the compositions in accordance with the invention at a level of from 0.0001% to 4% active enzyme by weight of the composition.

Amylases include, for example, α-amylases obtained from a special strain of B licheniformis, described in more detail in GB-1,269,839 (Novo). Preferred commercially available amylases include for example, those sold under the tradename Rapidase by Gist-Brocades, and those sold under the tradename Termamyl and BAN by Novo Industries A/S. Amylase enzyme may be incorporated into the composition in accordance with the invention at a level of from 0.0001% to 2% active enzyme by weight of the composition.

Lipolytic enzyme may be present at levels of active lipolytic enzyme of from 0.0001% to 2% by weight, preferably 0.001% to 1% by weight, most preferably from 0.001% to 0.5% by weight of the compositions.

The lipase may be fungal or bacterial in origin being obtained, for example, from a lipase producing strain of Humicola sp., Thermomyces sp. or Pseudomonas sp. including Pseudomonas pseudoalcaligenes or Pseudomas fluorescens. Lipase from chemically or genetically modified mutants of these strains are also useful herein. A preferred lipase is derived from Pseudomonas pseudoalcaligenes, which is described in Granted European Patent, EP-B-0218272.

Another preferred lipase herein is obtained by cloning the gene from Humicola lanuginosa and expressing the gene in Aspergillus oryza, as host, as described in European Patent Application, EP-A-0258 068, which is commercially available from Novo Industri A/S, Bagsvaerd, Denmark, under the trade name Lipolase. This lipase is also described in U.S. Patent 4,810,414, Huge-Jensen et al, issued March 7, 1989.

Surfactant Materials

The compositions of the present invention can additionally contain a surfactant system. Suitable surfactants for inclusion in the compositions of the invention generally have a lipophilic chain length of from about 8 to about 22 carbon atoms and can be selected from anionic, cationic, nonionic, amphoteric, zwitterionic surfactants and mixtures thereof.

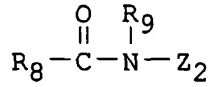
(i) Anionic Surfactants

Anionic surfactants suitable for inclusion in the compositions of the invention include alkyl sulphates, ethoxylated alkyl sulphates, alkyl glyceryl ether sulfonates, methyl acyl

taurates, fatty acyl glycinates, N-acyl glutamates, acyl isethionates, alkyl sulfosuccinates, alkyl ethoxysulphosuccinates, alpha-sulfonated fatty acids, their salts and/or their esters, alkyl ethoxy carboxylates, alkyl phosphate esters, ethoxylated alkyl phosphate esters, alkyl sulphates, acyl sarcosinates and fatty acid/protein condensates, and mixtures thereof. Alkyl and/or acyl chain lengths for these surfactants are C_{12}-C_{22}, preferably C_{12}-C_{18} more preferably C_{12}-C_{14}.

(ii) Nonionic Surfactants

The compositions of the invention can also comprise water-soluble nonionic surfactant(s). Surfactants of this class include C_{12}-C_{14} fatty acid mono-and diethanolamides, sucrose polyester surfactants and polyhydroxy fatty acid amide surfactants having the general formula below.

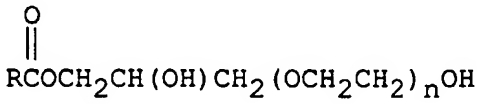


The preferred N-alkyl, N-alkoxy or N-aryloxy, polyhydroxy fatty acid amide surfactants according to the above formula are those in which R_8 is C_5-C_{31} hydrocarbyl, preferably C_6-C_{19} hydrocarbyl, including straight-chain and branched chain alkyl and alkenyl, or mixtures thereof and R_9 is typically hydrogen, C_1-C_8 alkyl or hydroxyalkyl, preferably methyl, or a group of formula $-R^1$-O-R^2 wherein R^1 is C_2-C_8 hydrocarbyl including straight-chain, branched-chain and cyclic (including aryl), and is preferably C_2-C_4 alkylene, R^2 is C_1-C_8 straight-chain, branched-chain and cyclic hydrocarbyl including aryl and oxyhydrocarbyl, and is preferably C_1-C_4 alkyl, especially methyl, or phenyl. Z_2 is a polyhydroxyhydrocarbyl moiety having a linear hydrocarbyl chain with at least 2 (in the case of glyceraldehyde) or at least 3 hydroxyls (in the case of other reducing sugars) directly connected to the chain, or an alkoxylated derivative (preferably ethoxylated or propoxylated) thereof. Z_2 preferably will be derived from a reducing sugar in a reductive amination reaction, most preferably Z_2 is a glycityl moiety. Suitable reducing sugars include glucose, fructose, maltose, lactose, galactose, mannose, and xylose, as well as glyceraldehyde. As raw materials, high dextrose corn syrup, high fructose corn syrup, and high maltose corn syrup can be utilised as well as the individual sugars listed above. These corn syrups may yield a mix of sugar components for Z_2. It should be understood that it is by no means intended to exclude other suitable raw materials. Z_2 preferably will be selected from the group consisting of $-CH_2-(CHOH)_n-CH_2OH$, $-CH(CH_2OH)-(CHOH)_{n-1}-CH_2H$, $CH_2(CHOH)_2(CHOR')CHOH)-CH_2OH$, where n is an integer from

1 to 5, inclusive, and R' is H or a cyclic mono- or polysaccharide, and alkoxylated derivatives thereof. As noted, most preferred are glycityls wherein n is 4, particularly -CH_2-$(CHOH)_4$-CH_2OH.

The most preferred polyhydroxy fatty acid amide has the formula $R_8(CO)N(CH_3)CH_2(CHOH)_4CH_2OH$ wherein R_8 is a C6-C19 straight chain alkyl or alkenyl group. In compounds of the above formula, R_8-CO-N< can be, for example, cocoamide, stearamide, oleamide, lauramide, myristamide, capricamide, palmiamide, tallowamide, etc.

Suitable oil derived nonionic surfactants for use herein include water soluble vegetable and animal-derived emollients such as triglycerides with a polyethyleneglycol chain inserted; ethoxylated mono and di-glycerides, polyethoxylated lanolins and ethoxylated butter derivatives. One preferred class of oil-derived nonionic surfactants for use herein have the general formula below:



wherein n is from about 5 to about 200, preferably from about 20 to about 100, more preferably from about 30 to about 85, and wherein R comprises an aliphatic radical having on average from about 5 to 20 carbon atoms, preferably from about 7 to 18 carbon atoms.

Suitable ethoxylated oils and fats of this class include polyethyleneglycol derivatives of glyceryl cocoate, glyceryl caproate, glyceryl caprylate, glyceryl tallowate, glyceryl palmate, glyceryl stearate, glyceryl laurate, glyceryl oleate, glyceryl ricinoleate, and glyceryl fatty esters derived from triglycerides, such as palm oil, almond oil, and corn oil, preferably glyceryl tallowate and glyceryl cocoate.

Preferred for use herein are polyethyleneglycol based polyethoxylated C_9-C_{15} fatty alcohol nonionic surfactants containing an average of from about 5 to about 50 ethyleneoxy moieties per mole of surfactant.

Suitable polyethylene glycol based polyethoxylated C_9-C_{15} fatty alcohols suitable for use herein include C_9-C_{11} Pareth-3, C_9-C_{11} Pareth-4, C_9-C_{11} Pareth-5, C_9-C_{11} Pareth-

6, C_9-C_{11} Pareth-7, C_9-C_{11} Pareth-8, C_{11}-C_{15} Pareth-3, C_{11}-C_{15} Pareth-4, C_{11}-C_{15} Pareth-5, C_{11}-C_{15} Pareth-6, C_{11}-C_{15} Pareth-7, C_{11}-C_{15} Pareth-8, C_{11}-C_{15} Pareth-9, C_{11}-C_{15} Pareth-10, C_{11}-C_{15} Pareth-11, C_{11}-C_{15} Pareth-12, C_{11}-C_{15} Pareth-13 and C_{11}-C_{15} Pareth-14. PEG 40 hydrogenated castor oil is commercially available under the tradename Cremophor (RTM) from BASF. PEG 7 glyceryl cocoate and PEG 20 glyceryl laurate are commercially available from Henkel under the tradenames Cetiol (RTM) HE and Lamacit (RTM) GML 20 respectively. C_9-C_{11} Pareth-8 is commercially available from Shell Ltd under the tradename Dobanol (RTM) 91-8. Particulary preferred for use herein are polyethylene glycol ethers of ceteryl alcohol such as Ceteareth 25 which is available from BASF under the trade name Cremaphor A25.

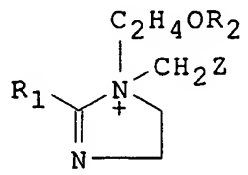
Also suitable for use herein are nonionic surfactants derived from composite vegetable fats extracted from the fruit of the Shea Tree (Butyrospermum Karkii Kotschy) and derivatives thereof. Similarly, ethoxylated derivatives of Mango, Cocoa and Illipe butter may be used in compositions according to the invention. Although these are classified as ethoxylated nonionic surfactants it is understood that a certain proportion may remain as non-ethoxylated vegetable oil or fat.

Other suitable oil-derived nonionic surfactants include ethoxylated derivatives of almond oil, peanut oil, rice bran oil, wheat germ oil, linseed oil, jojoba oil, oil of apricot pits, walnuts, palm nuts, pistachio nuts, sesame seeds, rapeseed, cade oil, corn oil, peach pit oil, poppyseed oil, pine oil, castor oil, soybean oil, avocado oil, safflower oil, coconut oil, hazelnut oil, olive oil, grapeseed oil, and sunflower seed oil.

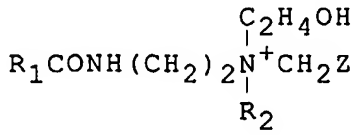
(iii) Amphoteric Surfactants

Amphoteric surfactants suitable for use in the compositions of the invention include:

(a) imidazolinium surfactants of formula (VII)



wherein R_1 is C_7-C_{22} alkyl or alkenyl, R_2 is hydrogen or CH_2Z, each Z is independently CO_2M or CH_2CO_2M, and M is H, alkali metal, alkaline earth metal, ammonium or alkanolammonium; and/or ammonium derivatives of formula (VIII)



wherein R_1, R_2 and Z are as defined above;

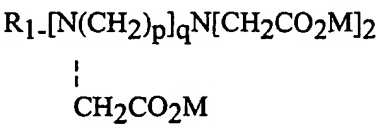
(b) aminoalkanoates of formula (IX)

$$R_1NH(CH_2)_nCO_2M$$

iminodialkanoates of formula (X)

$$R_1N[(CH_2)_mCO_2M]_2$$

and iminopolyalkanoates of formula (XI)



wherein n, m, p, and q are numbers from 1 to 4, and R_1 and M are independently selected from the groups specified above; and

(c) mixtures thereof.

Suitable amphoteric surfactants of type (a) are marketed under the trade name Miranol and Empigen and are understood to comprise a complex mixture of species. Traditionally, the Miranols have been described as having the general formula (VII), although the CTFA Cosmetic Ingredient Dictionary, 3rd Edition indicates the non-cyclic structure (VIII) while the 4th Edition indicates yet another structural isomer in which R_2 is O-linked rather than N-linked. In practice, a complex mixture of cyclic and non-cyclic

species is likely to exist and both definitions are given here for sake of completeness. Preferred for use herein, however, are the non-cyclic species.

Examples of suitable amphoteric surfactants of type (a) include compounds of formula XII and/or XIII in which R_1 is C_8H_{17} (especially iso-capryl), C_9H_{19} and $C_{11}H_{23}$ alkyl. Especially preferred are the compounds in which R_1 is C_9H_{19}, Z is CO_2M and R_2 is H; the compounds in which R_1 is $C_{11}H_{23}$, Z is CO_2M and R_2 is CH_2CO_2M; and the compounds in which R_1 is $C_{11}H_{23}$, Z is CO_2M and R_2 is H.

In CTFA nomenclature, materials suitable for use in the present invention include cocoamphocarboxypropionate, cocoamphocarboxy propionic acid, and especially cocoamphoacetate and cocoamphodiacetate (otherwise referred to as cocoamphocarboxyglycinate). Specific commercial products include those sold under the trade names of Ampholak 7TX (sodium carboxy methyl tallow polypropyl amine), Empigen CDL60 and CDR 60 (Albright & Wilson), Miranol H2M Conc. Miranol C2M Conc. N.P., Miranol C2M Conc. O.P., Miranol C2M SF, Miranol CM Special (Rhône-Poulenc); Alkateric 2CIB (Alkaril Chemicals); Amphoterge W-2 (Lonza, Inc.); Monateric CDX-38, Monateric CSH-32 (Mona Industries); Rewoteric AM-2C (Rewo Chemical Group); and Schercotic MS-2 (Scher Chemicals). Further examples of amphoteric surfactants suitable for use herein include Octoxynol-1 (RTM), polyoxethylene (1) octylphenyl ether; Nonoxynol-4 (RTM), polyoxyethylene (4) nonylphenyl ether and Nonoxynol-9, polyoxyethylene (9) nonylphenyl ether.

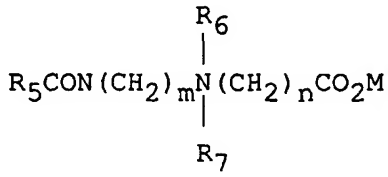
It will be understood that a number of commercially-available amphoteric surfactants of this type are manufactured and sold in the form of electroneutral complexes with, for example, hydroxide counterions or with anionic sulfate or sulfonate surfactants, especially those of the sulfated C_8-C_{18} alcohol, C_8-C_{18} ethoxylated alcohol or C_8-C_{18} acyl glyceride types. Note also that the concentrations and weight ratios of the amphoteric surfactants are based herein on the uncomplexed forms of the surfactants, any anionic surfactant counterions being considered as part of the overall anionic surfactant component content.

Examples of preferred amphoteric surfactants of type (b) include N-alkyl polytrimethylene poly-, carboxymethylamines sold under the trade names Ampholak X07 and Ampholak 7CX by Berol Nobel and also salts, especially the triethanolammonium salts and salts of N-lauryl-beta-amino propionic acid and N-lauryl-imino-dipropionic

acid. Such materials are sold under the trade name Deriphat by Henkel and Miratаine by Rhône-Poulenc.

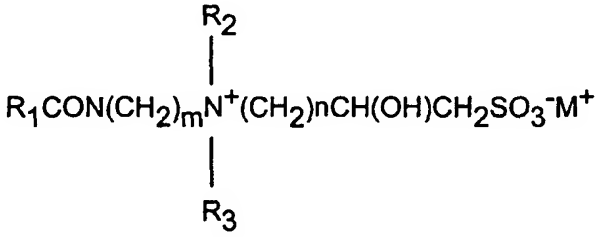
(iv) Zwitterionic Surfactants

Water-soluble auxiliary zwitterionic surfactants suitable for inclusion in the compositions of the present invention include alkyl betaines of the formula $R_5R_6R_7N^+(CH_2)_nCO_2M$ and amido betaines of the formula (XII) below:



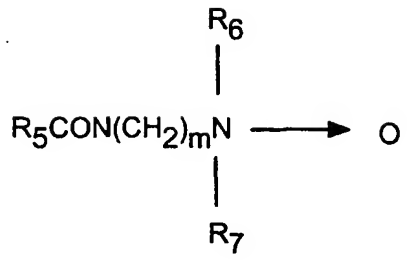
wherein R_5 is C_{11}-C_{22} alkyl or alkenyl, R_6 and R_7 are independently C_1-C_3 alkyl, M is H, alkali metal, alkaline earth metal, ammonium or alkanolammonium, and n, m are each numbers from 1 to 4. Preferred betaines include cocoamidopropyldimethylcarboxymethyl betaine, laurylamidopropyldimethylcarboxymethyl betaine and Tego betaine (RTM).

Water-soluble auxiliary sultaine surfactants suitable for inclusion in the compositions of the present invention include alkyl sultaines of the formula (XIII) below:



wherein R_1 is C_7 to C_{22} alkyl or alkenyl, R_2 and R_3 are independently C_1 to C_3 alkyl, M is H, alkali metal, alkaline earth metal, ammonium or alkanolammonium and m and n are numbers from 1 to 4. Preferred for use herein is coco amido propylhydroxy sultaine.

Water-soluble auxiliary amine oxide surfactants suitable for inclusion in the compositions of the present invention include alkyl amine oxide $R_5R_6R_7NO$ and amido amine oxides of the formula (XIV) below:



wherein R_5 is C_{11} to C_{22} alkyl or alkenyl, R_6 and R_7 are independently C_1 to C_3 alkyl, M is H, alkali metal, alkaline earth metal, ammonium or alkanolammonium and m is a number from 1 to 4. Preferred amine oxides include cocoamidopropylamine oxide, lauryl dimethyl amine oxide and myristyl dimethyl amine oxide.

Optional Materials

A number of additional optional materials can be added to the coloring compositions herein described each at a level of from about 0.001% to about 5%, preferably from about 0.01% to about 3%, more preferably from about 0.05% to about 2% by weight of composition. Such materials include proteins and polypeptides and derivatives thereof; water-soluble or solubilizable preservatives such as DMDM Hydantoin, Germall 115, methyl, ethyl, propyl and butyl esters of hydroxybenzoic acid, EDTA, Euxyl (RTM) K400, natural preservatives such as benzyl alcohol, potassium sorbate and bisabalol, benzoic acid, sodium benzoate and 2-phenoxyethanol; antioxidants such as sodium sulphite, hydroquinone, sodium bisulphite, sodium metabisulphite and thyoglycolic acid, sodium dithionite, erythrobic acid and other mercaptans; dye removers such as oxalic acid, sulphated castor oil, salicylic acid and sodium thiosulphate; H_2O_2 stabilisers such as tin compounds such as sodium stannate, stannic hydroxide and stannous octoate, acetanilide, phenacetin colloidal silica such as magnesium silicate, oxyquinoline sulphate, sodium phosphate, and tetrasodium pyrophosphate; and ρ-hydroxybenzoates; moisturising agents such as hyaluronic acid, chitin , and starch-grafted sodium polyacrylates such as Sanwet (RTM) IM-1000, IM-1500 and IM-2500 available from Celanese Superabsorbent Materials, Portsmith, VA, USA and described in US-A-4,076,663 as well as methyl cellulose, starch, higher fatty alcohols, paraffin oils, fatty acids and the like; solvents ; anti-bacterial agents such as Oxeco (phenoxy isopropanol); low temperature phase modifiers such as ammonium ion sources (e.g. NH_4 Cl); viscosity

control agents such as magnesium sulfate and other electrolytes; quaternary amine compounds such as distearyl-, dilauryl-, di-hydrogenated beef tallow-, dimethyl ammonium chloride, dicetyldiethyl ammoniumethylsulphate, ditallowdimethyl ammonium methylsulphate, disoya dimethyl ammonium chloride and dicoco dimethyl ammonium chloride; hair conditioning agents such as silicones, higher alcohols, cationic polymers and the like; enzyme stabilisers such as water soluble sources of calcium or borate species; colouring agents; TiO_2 and TiO_2-coated mica; perfumes and perfume solubilizers; and zeolites such as Valfour BV400 and derivatives thereof and Ca^{2+}/Mg^{2+} sequestrants such as polycarboxylates, amino polycarboxylates, polyphosphonates, amino polyphosphonates etc. and water softening agents such as sodium citrate.

The present invention is represented by the following non-limiting examples. In the examples, all concentrations are on a 100% active basis and all percentages are by weight unless otherwise stated and the abbreviations have the following designations:

Oxidising agent	hydrogen peroxide
Oxidative Dye 1	para-phenylene diamine
Oxidative Dye 2	2,5-diaminotoluene sulphate
Oxidative Dye 3	para-aminophenol
Oxidative Dye 4	resorcinol
Oxidative Dye 5	m-aminophenol
Oxidative Dye 6	m-phenylenediamine
Oxidative Dye 7	2-amino-3-hydroxypyridine
Oxidative Dye 8	1-naphthol
Oxidative Dye 9	4-amino-2-hydroxytoluene
Chelating agent	tetrasodium EDTA
Surfactant 1	Ceteareth-25
Thickener 1	Cetyl alcohol
Thickener 2	Stearyl alcohol
Alkali 1	Ammonium carbonate
Solvent	Dipropylene glycol

Examples I - XV

The following are hair treatment compositions in the form of hair coloring compositions which are representative of the present invention.

Ingredient	I	II	III	IV	V	VI	VII	VIII
Oxidising Agent	3	3	3	3	3	4.5	3	4.5
Oxidative Dye 1	0.85	0	0	0.37	0	0	0.75	0
Oxidative Dye 2	0	0.43	0.5	0	0	0.1	0	0.09
Oxidative Dye 3	0	0.16	0	0.25	0.4	0.1	0	0.02
Oxidative Dye 4	0.21	0.05	0	0.2	0	0.8	0.27	0.04
Oxidative Dye 5	0.21	0.05	0	0.9	0	0.005	0.15	0.008
Oxidative Dye 6	0.05	0	0	0	0	0	0.01	0.001
Oxidative Dye 7	0	0	0	0	0	0	0	0
Oxidative Dye 8	0	0	0	0	0.11	0	0	0
Oxidative Dye 9	0	0.25	0.25	0.7	0.16	0.0025	0	0
Chelating Agent	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Antioxidant 1	0.2	0.2	0.2	0.2	0.2	0.1	0.2	0.2
Antioxidant 2	0.5	0.5	0.25	0.25	0.5	0.1	0.5	0.5
Surfactant 1	1.5	1.5	1.5	2.1	1.5	1.5	2.1	1.5
Thickener 1	2.25	2.25	2.25	3.12	2.25	2.25	3.12	2.25
Thickener 2	2.25	2.25	2.25	3.12	2.25	2.25	3.12	2.25
Alkali 1	3	3	3	3	3	4	3	4
Solvent	0	3	3	0	3	0	0	0
Water	to 100	to 100	to 100	to 100	to 100	to 100	to100	to100
pH	8.9	8.8	8.9	8.9	8.9	8.9	8.9	8.9

Ingredient	IX	X	XI	XII	XIII	XIV	XV
Oxidising Agent	3	3	3	3	3	4.5	4.5
Oxidative Dye 1	0	0.3	0.55	0	0.16	0	0
Oxidative Dye 2	0.3	0	0	0.26	0	0.03	0.1
Oxidative Dye 3	0.3	0.05	0	0.19	0.12	0.16	0.05
Oxidative Dye 4	0.05	0.14	0.05	0.16	0.15	0.05	0.05
Oxidative Dye 5	0	0.025	0.09	0.01	0.02	0	0.005
Oxidative Dye 6	0	0	0.13	0	0	0	0

Oxidative Dye 7	0	0	0.1	0	0	0	0
Oxidative Dye 8	0.13	0	0.04	0	0	0	0.015
Oxidative Dye 9	0.16	0	0	0.013	0.025	0.06	0.001
Chelating Agent	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Antioxidant 1	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Antioxidant 2	0.5	0.5	0.5	0.5	0.5	0.2	0.2
Surfactant 1	1.5	1.5	2.1	1.5	1.5	1.5	1.5
Thickener 1	2.25	2.25	3.12	2.25	2.25	2.25	2.25
Thickener 2	2.25	2.25	3.12	2.25	2.25	2.25	2.25
Alkali 1	3	3	3	3	3	4	4
Solvent	3	0	1	1	1	1.5	1
Water	to 100	to 100	to 100	to 100	to 100	to 100	to100
pH	8.9	8.9	8.9	8.8	8.9	8.9	8.8

In the examples above, water is used as the diluent. However in variations hereof water can be replaced, in part, by from about 0.5% to about 50% by weight of the total water content of the examples by diluents such as lower alcohols, e.g., ethylene glycol, ethylene glycol monoethyl ether, diethylene glycol, diethylene glycol monoethyl ether, propylene glycol, 1,3-propanediol, ethanol, isopropyl alcohol, glycerine, butoxyethanol, ethoxydiglycol, hexylene glycol, polyglyceryl-2-oleyl ether and mixtures thereof.

Examples I-XV provide a complete range of colours, i.e. from blondes to blacks, while reducing skin irritation, hair damage and odor. The compositions of the examples also provide excellent grey coverage.

Method of use

It is important that dyeing compositions be in a form which is easy and convenient to prepare and use by the consumer, since the oxidising agent must remain in contact with the hair for a certain period of time and not run or drip off of the hair, possibly causing eye or skin irritation.

To address the above, the coloring compositions of the present invention can be provided in both a single pack or in kit form as separately packaged components to maintain stability, and, if so desired, either mixed by the user immediately prior to application to

the hair, or mixed and stored for future use, or mixed and partly used and the remainder stored for future use.

As hereinbefore described, the compositions according to the present invention may be used by the consumer as a single component package. Such a single pack would comprise a single solution at pH 7 to 9 containing the oxidising agent, the hair coloring agent and the ammonium carbonate and/or ammonium carbamate. The solution would be applied directly to the hair by the consumer without the need for any pretreatments or mixing thereby providing a simple, fast, easy to use, 'no-mess' hair coloring system. A further advantage of such a single component system is that it could be stored and re-used i.e., a single package could contain enough coloring composition for several applications over time.

Thus, according to a further aspect of the present invention, there is provided a method for bleaching and coloring hair wherein a hair bleaching and coloring composition is applied directly to the hair and wherein the hair bleaching and coloring composition comprises:

(a) an oxidising agent;
(b) an oxidative or non-oxidative hair coloring agent; and
(c) ammonium carbonate and/or ammonium carbamate;

wherein the composition has a pH of from about 7 to about 9.

The coloring compositions herein are applied to the hair for periods of from 1 minute to 60 minutes depending upon the degree of coloring required. A preferred time is between 5 minutes and 30 minutes. The coloring compositions according to the present invention can be applied to both wet and dry hair.

According to a still further aspect of the present invention, there is provided a method for bleaching and coloring hair comprising the steps of applying to the hair a first component comprising an oxidising agent followed by applying to the hair a second component comprising an oxidative and/or non-oxidative hair coloring agent in combination with ammonium carbonate and/or ammonium carbamate. In addition the present invention provides a method for bleaching and coloring the hair comprising the steps of applying to the hair a first component comprising an oxidative and/or non-oxidative hair coloring

agent in combination with ammonium carbonate and/or ammonium carbamate followed by applying to the hair a second component comprising an oxidising agent.

Kits

According to the present invention there is also provided a hair coloring kit wherein the kit comprises two or more separate components. In preferred embodiments the kit components are admixed to form a coloring composition prior to application to the hair. In alternative embodiments, the individual components can be applied separately to the hair in a sequential manner.

A preferred kit herein comprises at least two components, a first component containing a combination of an oxidative and/or non-oxidative hair coloring agent and ammonium carbonate and/or ammonium carbamate and a second component comprising an oxidising agent. The components can either be mixed by the user immediately prior to application to the hair or can be applied separately. The components can also be mixed and the resulting composition can be stored for future use or part of the resulting composition can be used and the rest of the composition stored for future use. In one embodiment of the present invention the oxidising component comprises a stabilised aqueous solution of an inorganic peroxygen oxidising agent, most generally hydrogen peroxide in an amount such that the final concentration of the coloring composition for use on the hair is from about 0.05% to about 6% by weight and additional agents as herein before described.

Examples of such kits are as follows:

I. A hair coloring kit is assembled comprising a single package including therein: (1) a 50 ml bottle of hydrogen peroxide (6% by weight of H_2O_2), and optionally buffering agents and/or stabilisers; and (2) a 50 ml bottle containing one or more oxidative hair coloring agents, ammonium carbonate and/or ammonium carbamate and, optionally, additional agents such as surfactants, stabilisers, buffering agents, antioxidants, thickeners etc. The component containing the oxidative hair coloring agents and ammonium carbonate and/or carbamate can either be admixed with the hydrogen peroxide to form the dyeing system of the present invention and the resulting solution can be either applied to the hair to color it or stored for future use, or the separately packaged stable components can be stored and mixed when required.

II. A hair coloring kit as described in I above wherein the hydrogen peroxide containing component is applied to the hair prior to application of the oxidative hair coloring agents, ammonium carbonate and/or ammonium carbamate and additional materials to the hair.

III. A hair coloring kit as described in I above wherein the hydrogen peroxide containing component is applied to the hair after application of the oxidative hair coloring agents, ammonium carbonate and/or ammonium carbamate and additional materials to the hair.

IV Further examples of kit components for the hair coloring compositions according to the present invention include separately packaged oxidant component and a separately packaged oxidative hair coloring agent component comprising hair coloring agent and ammonium carbonate and/or ammonium carbamate wherein either one or both components are present in particulate form.

What is Claimed is:

1. A hair bleaching and coloring composition comprising:

   (a) an oxidising agent;
   (b) an oxidative or non-oxidative hair coloring agent; and
   (c) ammonium carbonate and/or ammonium carbamate;

   wherein the pH of the composition is from about 7 to about 9.

2. A composition according to Claim 1 wherein the pH of the composition is in the range of from about 7.25 to about 9.0, preferably from about 7.75 to about 9.0, more preferably from about 8 to about 9, most preferably from about 8.25 to about 9.

3. A composition according to Claim 1 or 2 wherein the oxidising agent is an inorganic peroxygen oxidising agent.

4. A composition according to any of Claims 1 to 3 wherein the inorganic peroxygen oxidising agent is present at a level of 0.01% to less than about 6%, preferably from about 0.01% to about 4%, more preferably from about 1% to about 4%, more preferably from about 2% to about 3% by weight of composition.

5. A composition according to any of Claims 1 to 4 wherein the oxidising agent is hydrogen peroxide.

6. A composition according to any of Claims 1 to 5 wherein the coloring agent is an oxidative coloring agent.

7. A composition according to Claim 6 wherein the total level of oxidative hair coloring agent is from about 0.001% to about 5%, preferably from about 0.01% to about 4%, more preferably from about 0.1% to about 3%, most preferably from about 0.1% to about 1% by weight.

8. A composition according to Claim 6 or 7 wherein each oxidative hair coloring agent is present at a level of from about 0.001% to about 3%, preferably from about 0.01% to about 2% by weight.

9. A composition according to any of Claims 1 to 8 which is substantially free of additional buffering agents and pH modifiers.

10. Use of a composition according to any of Claims 1 to 9 for bleaching and coloring human or animal hair.

11. A method for bleaching and coloring human or animal hair comprising applying to the hair a hair bleaching and coloring composition according to any of Claims 1 to 9.

12. A hair bleaching and coloring kit comprising at least two components, a first component comprising an oxidising agent and a second component comprising a combination of a hair coloring agent and ammonium carbonate and/or ammonium carbamate.

13. A method for bleaching and coloring human or animal hair comprising the steps of applying to the hair a first component followed by applying the hair a second component, wherein the first component comprises an oxidising agent and wherein the second component comprises a combination of a hair coloring agent and ammonium carbonate and/or carbamate.

14. A method for bleaching and coloring human or animal hair comprising the steps of applying to the hair a first component followed by applying a second component, the first component comprising a combination of a hair coloring agent and ammonium carbonate and/or carbamate and the second component comprising an oxidising agent.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 00/28904

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 A61K7/13

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	DE 197 21 797 C (GOLDWELL GMBH) 3 September 1998 (1998-09-03) tables	1-10
A	EP 0 609 796 A (GOLDWELL AG) 10 August 1994 (1994-08-10) claims	1-10

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

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Date of the actual completion of the international search	Date of mailing of the international search report
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Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Pelli Wablat, B

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
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